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16 ABSTRACT

The effect of formaldehyde as a preservative for milk prior to radiochemical analysis for ^{131}I was studied. Results suggest that the formaldehyde concentration is critical and that at low formaldehyde concentrations (<0.5 M) significant protein binding of iodine occurs. Various alternatives for preserving milk prior to analysis for ^{131}I and stable iodide by the specific ion electrode method are presented.

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Status of Iodine in Formaldehyde-Preserved Milk—Revisited

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To assess potential radiation exposures of individuals near nuclear power stations, the U.S. Nuclear Regulatory Commission (NRC) has established guidelines (USNRC74) for measuring ^{131}I in milk at concentrations of 0.35 pCi/l. The recommended method, based on a New York Department of Health method (Gu74), involves the addition of 20 mg of iodide carrier to 4 l of raw milk and preconcentration of iodine on anion-exchange resin. Iodine is stripped from the resin and precipitated as palladium iodide for chemical yield determination and counting. Most procedures currently used for monitoring ^{131}I in milk employ an initial anion-exchange concentration step, which is based on observations that 90 to 100% of the ^{131}I is present as iodide and recoverable by ion exchange (Mu61; Br72). Although the NRC method does not include the contribution from natural iodide in milk for the chemical yield determination (natural in contrast to carrier), recent studies show that this may seriously overestimate chemical recoveries (Ma75; Ke77). Natural iodide levels in milk fluctuate considerably depending on dairy practices and seasons, and may range from 2 to 6000 μg/l (Ma75). The addition of sufficient iodide carrier to insure that the natural iodide contribution is negligible will generally not be feasible as this would result in a very thick final precipitate not suitable for counting. A determination of the iodide concentration before or after carrier addition will generally be necessary.

In most monitoring situations, milk samples are preserved with formaldehyde to prevent spoilage during shipping, as field concentration by ion exchange is usually impracticable. Murthy, however, showed that formaldehyde can convert up to 98% of the iodide to protein-bound iodine (PBI) which is not recoverable by anion exchange (Mu62). The transformation of I^- to PBI results from the oxidation of formaldehyde to hydrogen peroxide by xanthine oxidase in milk. Hydrogen peroxide oxidizes I^- to I_2, which combines with protein to form PBI. Reaction rates from the conversion of I^- to PBI in raw milk were studied as functions of temperature, formaldehyde concentration, xanthine oxidase activity, and I^- concentration (Mu66). Reaction rates increased with formaldehyde concentration from 1.3×10^{-5}/s to 1.3×10^{-4}/s, with increasing iodide concentration up to 2.5 mg/l, with increasing xanthine oxidase activity, and with temperature from 40°C to 60°C. At temperatures above 75°C no PBI was formed due to denaturation of xanthine oxidase.

Recent studies by Thomas have shown that formaldehyde could be used for preservation of milk samples prior to ^{131}I analysis by anion-exchange (Th76). Raw milk was preserved by the addition of a mixture of 80 ml of 37% formaldehyde (0.25 M formaldehyde), 20 mg of iodide carrier, and a few drops of 1 M sodium bisulfite to 4 l of milk. The recoveries of ^{131}I using this technique were comparable to recoveries from unpreserved milk, suggesting that conversion to PBI did not occur under these conditions; however, the formaldehyde concentration was an order of magnitude higher than the highest concentration "investigated" by Murthy (Mu66).

Failure to consider the effect of PBI formation in formaldehyde-preserved milk could lead to incorrect ^{131}I measurements. If formaldehyde is added before carrier iodide, exchange of ^{131}I and carrier iodide might not be achieved. This would introduce errors in the chemical recovery correction factor. The formation of PBI after equilibration of ^{131}I and stable iodide would not effect the accuracy of the measurement if the total iodine concentration (iodide and PBI) is determined; however, it could result in a lower chemical yield which decreases the precision at low ^{131}I concentrations. In the absence of significant PBI formation, only the stable iodide concentration has to be determined. Stable iodide concentrations in milk can be measured by the specific iodide technique which is rapid and inexpensive (Cr75).

These investigations were initiated to study the effect of formaldehyde preservation of raw milk in view of the differences observed by Murthy (Mu62; Mu66) and Thomas (Th76), and to determine if the specific iodide electrode method could be used for iodide analysis of formaldehyde-preserved milk.

Recovery of ^{131}I from Formaldehyde-Preserved Milk by Anion Exchange

Fresh raw milk from a local dairy was spiked with carrier-free ^{131}I (Na ^{131}I in NaOH) and stored at 5°C to prevent spoilage. Solutions of KI were prepared from reagent grade chemicals. Reagent

grade formaldehyde (37% solution) was used. The stable iodide concentration in raw milk was determined by the iodide electrode method described below.

Samples of ^{131}I-spiked raw milk were preserved by addition of a mixture of formaldehyde, potassium iodide, and 1×10^{-2} M $NaHSO_3$. Formaldehyde concentrations ranged from 1.2×10^{-1} M to 7.5×10^{-1} M and iodide concentrations ranged from 0.1 to 5.3 mg/l. The $NaHSO_3$ concentration was 2.5×10^{-3} M. The milk temperature at the time of formaldehyde addition was not controlled and varied from about 10 to 25°C. After storage of the milk for 7 days at room temperature (~ 23°C), 50 ml aliquots were removed and stirred with 10 g of anion-exchange resin (Dowex 1 × 8, Cl⁻ form, 25–50 mesh) for 1 hr. The resin was collected by filtration through a sintered-glass crucible and washed with 50 ml of warm distilled water. The ^{131}I in the resin and the milk plus wash fraction was determined by gamma spectroscopy.

The recoveries of ^{131}I by anion exchange from milk preserved with formaldehyde and $NaHSO_3$ at the concentrations recommended by Thomas (Th76) were determined at stable iodide concentrations of 0.3, 2.3 and 5.3 mg/l. At concentrations of 2.3 and 5.3 mg/l., the recoveries were high and averaged 95% compared to 96–97% recovery from unpreserved milk; however, at 0.3 mg/l the recoveries were highly variable and averaged only 66 ± 17%.

These results suggest that preservation of milk by the Thomas procedure does not result in conversion of iodide to PBI^1 and that PBI^1 formation is a function of stable iodide concentration. Modification of the Thomas preservative procedure by adding smaller quantities of iodide carrier or eliminating it could lead to substantial conversion of iodide to PBI^1.

The recovery of ^{131}I from preserved milk by anion exchange as a function of formaldehyde and iodide concentration is presented in Table 1. As large variations were about 20 for milk at the same formaldehyde and iodide concentrations, the range of recoveries is given. These variations were initially attributed to possible differences in xanthine oxidase activity in different batches of milk; however, subsequent measurements (discussed in the next section) showed that the variations may be due to differences in milk temperature at the time formaldehyde was added.

The effect of formaldehyde concentration was quite dramatic at all iodide concentrations. Iodine-131 recoveries from milk preserved with formaldehyde at 1.2×10^{-1} M were less than 15% at iodide concentrations ranging from 0.3 mg/l to 5.3 mg/l. These results are in agreement with earlier work by Murthy which showed that greater than 98% of the ^{131}I in milk was converted to PBI^1 at a formaldehyde concentration of 1.3×10^{-1} M (Mu62). The data are too variable for predicting the amount of protein binding of iodide in milk as a function of the formaldehyde and iodide concentration; however, the results show that protein binding of iodide decreases with increasing formaldehyde concentrations above 1.3×10^{-1} M, and that the protein binding of iodide is related to both the formaldehyde and iodide concentration.

Table 1. Effect of formaldehyde and iodide concentrations on milk ^{131}I [illegible]

Formaldehyde concentration (molarity)	Percent ^{131}I recovered by anion exchange from milk containing: 0.3 mg/l I⁻	2.3 mg/l I⁻	5.3 mg/l I⁻
[illegible]	[illegible]	[illegible]	[illegible]

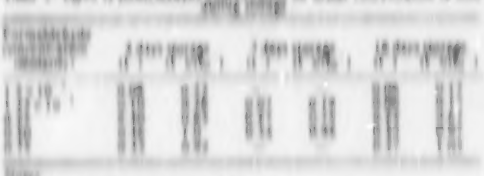
[1] Data derived at 7 days at room temperature. [illegible] to 25°C at room temperature after formaldehyde addition.

Stable Iodide Measurements of Formaldehyde-Preserved Milk

Iodide concentrations in milk were measured with an Orion iodide electrode (94-53), using a single junction reference electrode, and digital voltmeter (701). Measurements were made by the standard addition technique of determining the change in electrode potential before and after adding a known quantity of KI to 25 ml of milk (Ob73).

The iodide content of raw milk samples was measured before addition of formaldehyde or iodide carrier. The conversion of iodide to PBI^1 in milk as a function of both formaldehyde concentration and storage time was determined by adding formaldehyde and storing at room temperature. Aliquots of the samples were removed after appropriate storage time for iodide determinations.

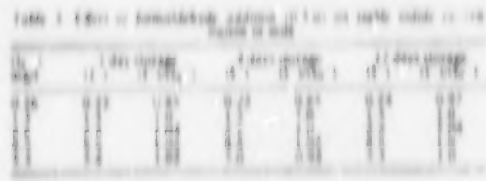
The iodide concentration of formaldehyde-preserved milk was determined for milk containing 0.36 mg/l of iodide with a formaldehyde concentration range of 0.015 M–0.75 M. The results are given in Table 2. At concentrations of 0.015, 0.12 and 0.29 M, the iodide losses after 18 days storage were 83, 81 and 13%, respectively. Iodide losses at formaldehyde concentrations of 0.50 and 0.75 M were negligible. The conversion of iodide to PBI^1 was inhibited at high formaldehyde concentrations (> 0.5 M), which suggests that xanthine oxidase is denatured or deactivated at high formaldehyde concentrations. These results indicated that preservation of raw milk at a formaldehyde concentration

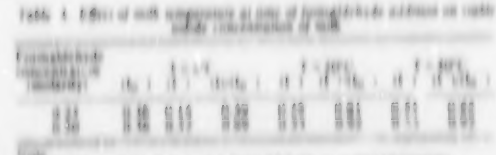


of 0.5 M did not lead to appreciable iodide losses due to CH_3I formation even at low iodide concentrations.

The preservation of milk at 0.5 M formaldehyde concentration was tested with raw milk containing from 0.36 mg/l to 5.3 mg/l of iodide. Iodide concentrations after 1, 4 and 12 days of storage are presented in Table 3. Comparison of the iodide concentrations of formaldehyde-preserved milk after 12 days of storage with the initial concentrations show that iodide losses were negligible except at the lowest concentration of 0.36 mg/l, where losses from 8 to 15% were observed during the 12-day storage period.

The effect of milk temperature at the time of formaldehyde addition was investigated by adjusting the temperature of raw milk (0.33 mg/l I^-) to 5, 20 and 40°C, adding appropriate quantities of formaldehyde, and measuring the stable iodide concentrations after storing for 7 days at room temperature. The results are presented in Table 4 and show that iodide losses in milk at 0.25 M formaldehyde concentration are much higher at lower temperatures. These results suggest that deactivation or denaturation of xanthine oxidase is related to both the formaldehyde concentration and the milk temperature when formaldehyde is added.





Conclusion

The results presented in this report are based on studies using raw milk from the Cincinnati, Ohio area. Milk from other areas may differ in xanthine oxidase activity, stable iodide concentration, and other constituents that could affect protein binding of formaldehyde-preserved milk. If formaldehyde is used to preserve milk for ^{131}I analysis, the effectiveness during shipping should be tested.

Several alternatives for milk preservation are available. Heat treatment before addition of formaldehyde will prevent protein binding of iodine. This may be accomplished by heating the milk to 75°C for 5 min. Milk can also be preserved by freezing. Both of these methods are somewhat inconvenient for preserving large volumes of milk for shipment to laboratories for analysis as they require additional equipment or material in the field.

The Thomas preservation technique for 4-l milk samples for ^{131}I analysis was found to be acceptable, and an aliquot of the formaldehyde-preserved milk can be analyzed for total iodide concentration by the electrode method. Milk samples may also be preserved for stable iodide measurement (without iodide carrier addition) by addition of formaldehyde at 0.5 M concentration.

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